Supplemental Information

Effects of Multiple-Bond Ruptures on Kinetic Parameters Extracted from Force Spectroscopy Measurements: Revisiting Biotin-Streptavidin Interactions

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Extended Freely Jointed Chain model

The loading rate depends on the dynamics of force applied to the bond. Often the loading rate is considered constant for simplicity in the data analysis. However, the polymeric tethers are unharmonic springs and the loading rate can be calculated more accurately by using different models of polymer dynamics (1,2). Force spectroscopy experiments are often conducted using constant probe velocity. In these experiments the motion of the probe base is split between the cantilever deflection and the elongation of polymeric tether. Therefore $\Delta z = v \cdot t = F/k_c + l(F)$ where Δz is the change in the probe position, v is the probe base velocity, F is the force applied to the molecular bond, k_c is the spring constant of the force sensor (cantilever in AFM experiments), and $l(F)$ is the force-dependent length of the tether. Thus the instantaneous loading rate is given by

$$\dot{F} = \left((v \cdot k_c)^{-1} + l'(F)/v \right)^{-1} \tag{S1}$$

Here prime denotes differentiation with respect to force. Elongation of the tether can be calculated by applying appropriate polymer chain models such as the freely jointed chain (FJC) or the worm-like chain (WLC) models (1-3). The dynamics of PEG tethers differ noticeably from the FJC model because of the proposed conformational transition between helical and planar forms (4). In this study we use PEG tethers, therefore the extended FJC model (eFJC) that was developed by Gaub et al. to model PEG chain extension in aqueous media (4) is used in the data analysis. According to this model the end-to-end length of the PEG tether can be calculated by (4,5)

$$l(F) = L_{max} \left(\left(e^{\Delta G(F)/k_B \cdot T} + 1 \right)^{-1} + \left(e^{-\Delta G(F)/k_B \cdot T} + 1 \right)^{-1} L_h / L_p \right) \cdot \left(\coth(\beta) - 1/\beta \right) \tag{S2}$$

Here L_h is the PEG monomer length at helical conformation (0.28 nm), L_p is the monomer length at planar conformation (0.36 nm), L_{max} is the maximum extension of the chain with N monomers that equals to $N \cdot L_p$; $\Delta G(F) = \Delta G_0 - F \cdot (L_p - L_h)$ with $\Delta G_0 = 3\ k_B T$, and $\beta = F \cdot l_K / (k_B T)$ where l_K

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is the Kuhn length and k_BT is the thermal energy. In Eq. S2 the distortion of the bond angles under force is neglected because for typical forces of biotin-streptavidin bond rupture (~100 pN) the associated distortion of the typical 3.5 kDa PEG chain contributes an elongation of ~1 Å, which is negligible in comparison to the chain length (~30 nm).

References:

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